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RAPID COMMUNICATION

H₃PO₄ in a Direct Synthesis of Oligo–Poly(ethylene phosphate) from Ethylene Glycol

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INTRODUCTION

There are several well-known procedures for preparing high-molar-mass polyesters of phosphoric acid, mostly in nucleic and teichoic acid chemistry. Particularly efficient methods are based on biochemical methods, such as polymerase chain reaction.¹ On the other hand, methods for the synthesis of linear poly(alkylene phosphate)s devoid of side groups are not simple, particularly when a larger scale is considered. These polymers of higher and medium molar masses could find numerous applications if acceptable synthetic methods were available. The first high-molar-mass linear poly(alkylene phosphate)s, devoid of side groups, were prepared in our laboratory with either coordinate ring-opening polymerization or transesterification processes. The same approaches could be used for the synthesis of oligomers with well-defined end groups.^{2–4}

The esterification of simple alcohols with H₃PO₄ or its derivatives, such as P₄O₁₀ and poly(phosphoric acid), is well known.⁵ For instance, the esterification of simple alcohols with H₃PO₄ was previously

described (e.g., the esterification of dodecyl alcohol),⁶ but the authors stressed that only traces of diesters of phosphoric acid were detected. Surprisingly, only POCl₃ was used for polymer preparation, but mostly branched, ill-defined oligomers were reported.⁷ High-molar-mass, linear or highly branched polyesters of phosphoric acid were also prepared by the reaction of phosphoric acid with some diepoxides in our earlier work.⁸

EXPERIMENTAL

Reaction of H₃PO₄ with Ethylene Glycol in Bulk

H₃PO₄ (5 g, 0.05 mol), ethylene glycol (4.9 g, 0.079 mol), and Sc(OSO₂CF₃)₃ as a catalyst (0.05 wt %) were placed in a heated flask equipped with a magnetic stirrer and a tube introducing dry argon under the surface of the reaction mixture. The flow rate was set to about 1 mL/s. The temperature was kept constant (at 120 °C). Argon flowing out from the system was directed to a trap cooled with dry ice, and the accumulated volatile products (mainly H₂O) were analyzed by NMR at different stages of the process, together with samples of the reaction mixture. The progress of esterification was monitored by ³¹P{¹H} NMR spectroscopy. The reaction

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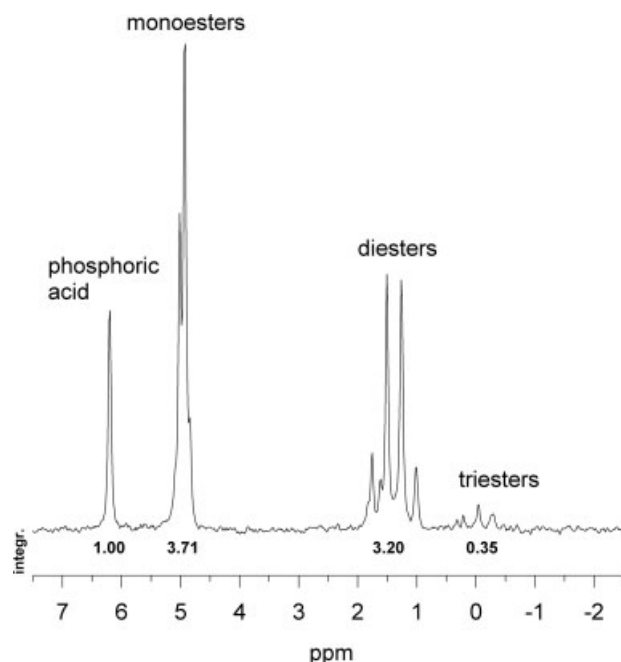


Figure 1. ^{31}P NMR spectrum of the polycondensation product of ethylene glycol with H_3PO_4 ($[\text{1}]_0/[\text{2}]_0 = 1.57$, temperature = 100°C , $\text{Sc}(\text{OSO}_2\text{CF}_3)_3$ catalyst concentration = 0.7 mol %).

was terminated when practically no more changes in the reaction mixture composition were observed.

Reaction of H_3PO_4 with Ethylene Glycol (H_2O Removed Azeotropically)

The reaction was carried out similarly, but instead of argon inlet and outlet tubes, the flask was equipped with an azeotropic unit (similar to a Dean–Stark water trap) for removing H_2O from the reaction system with the refluxing solvent (heptane, benzene, toluene, or xylene). About 50 mL of the solvent was added to the flask, and the system was kept at the temperature suitable for vigorous refluxing.

RESULTS AND DISCUSSION

Our first attempts at directly reacting the simplest glycol, namely ethylene glycol, with H_3PO_4 were unsuccessful. We then realized that for this reaction there is a relatively narrow temperature window and that some catalysts allow cleaner reactions, leading to medium-molar-mass oligo(ethylene phosphate)s rather than poly(ethylene phosphate)s.

Thus, we report here our first results, showing that the direct condensation of H_3PO_4 with ethylene glycol,

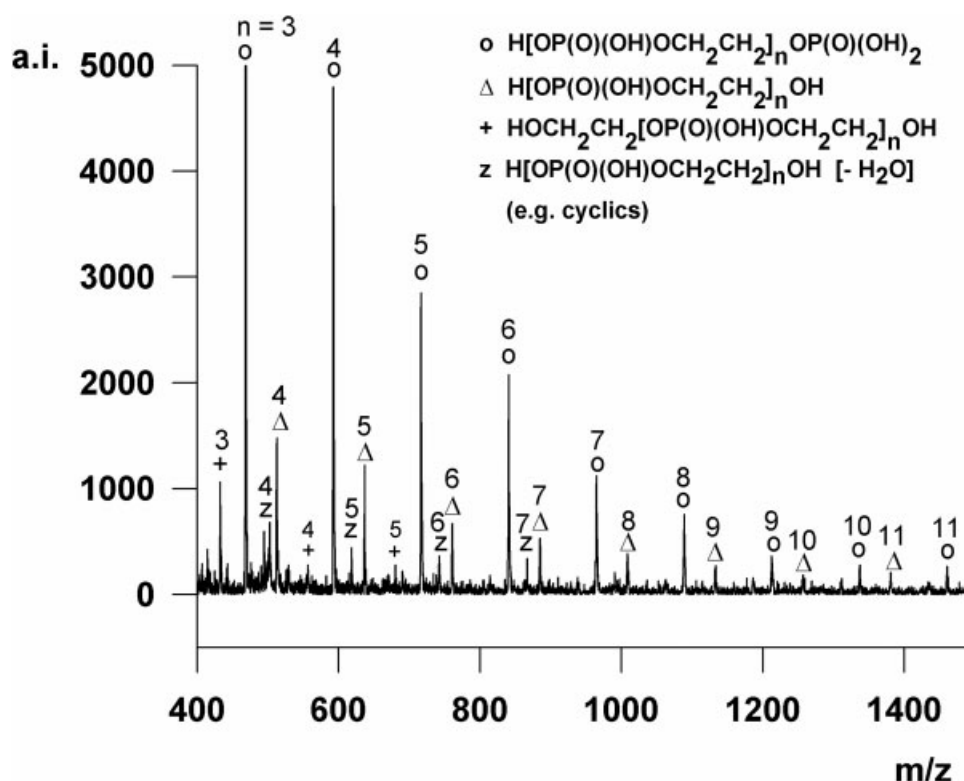
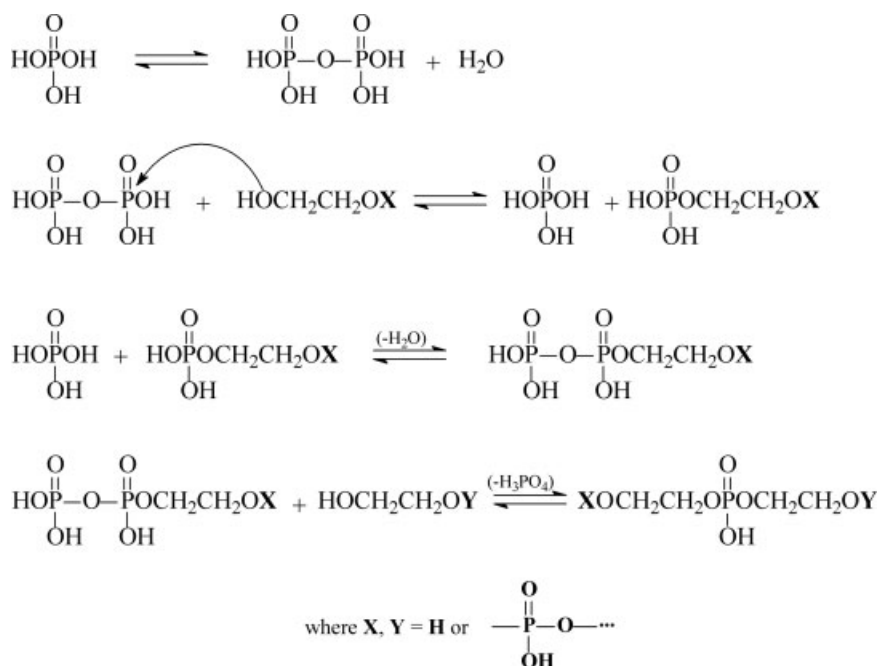


Figure 2. MALDI-TOF MS of the polycondensation product of ethylene glycol with H_3PO_4 ($[\text{1}]_0/[\text{2}]_0 = 1.62$, temperature = 98°C , $\text{Sc}(\text{OSO}_2\text{CF}_3)_3$ catalyst concentration = 0.1 mol %).



Scheme 1. Schematic course of the polyesterification of ethylene glycol with H_3PO_4 .

particularly in the presence of a catalyst such as $\text{Sc}(\text{OTf})_3$, which has been reported to be a good catalyst for the esterification of carboxylic acids with alcohols under mild conditions,⁹ leads to linear macromolecules of moderate molar masses. The formation of higher polymers is hampered by the dealkylation process, as revealed in this communication. If, however, the temperature is too high, then 1,4-dioxane and oligo(ethylene glycol)s are formed as side products. The polycondensation with ethylene glycol is by no means the only system providing poly(alkylene phosphate)s. A description of other syntheses will be given in our forthcoming full article.

Some glycols give, however, completely different products in the reaction with H_3PO_4 ; for instance, neopentyl glycol (2,2-dimethyl-propandiol-1,3) gives almost quantitatively 2-methylbutyraldehyde, that is, the same product formed in the reaction with H_2SO_4 .¹⁰

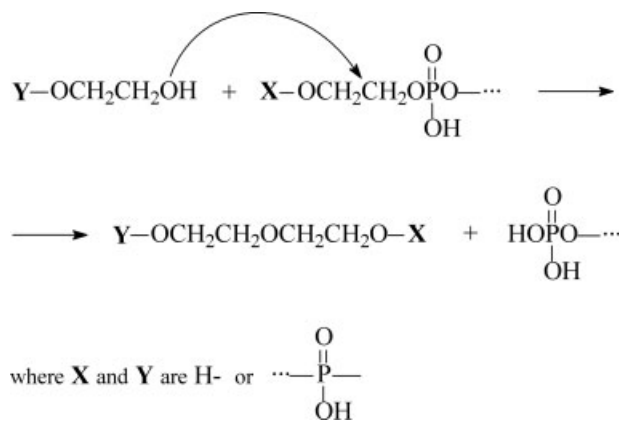
Thus, in this communication, we confine ourselves to only one system, namely ethylene glycol and phosphoric acid.

Polycondensation was carried out either under homogeneous conditions in bulk or under heterogeneous conditions in the presence of a hydrocarbon solvent, such as toluene at its boiling point, with the continuous removal of water, mostly in the presence of catalysts and in an atmosphere of an inert gas, and was followed by ^{31}P NMR analysis. A typical spectrum of the reaction mixture at the early stage of the reaction is shown in Figure 1. Assignments are given in the figure.

The ^{31}P NMR spectra are clean and show almost exclusively the presence of mono- and diesters. In some

polycondensation products, some triesters (branching points; cf. Fig. 1) are also present. We describe in this short note only major facts; therefore, we do not analyze the origin of the multiplets in the NMR spectrum, which are due to the different chemical environments of the P atoms in mono- and diesters. The following structures of macromolecules were observed by matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS), as shown in Figure 2.

Either two end groups are the same or two different ones are present in a given macromolecule. In some macromolecules, units of di- and triethylene glycols are also present.



Scheme 2. Formation of oligo(ethylene glycol)s by the wrong addition.

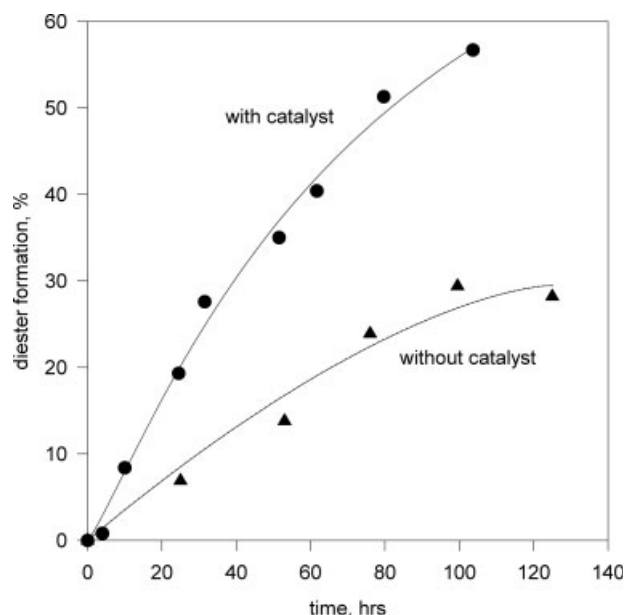


Figure 3. Course of polycondensation with and without a catalyst (conditions: $[1]_0/[2]_0 = 1.57$ with 0.7 mol % $\text{Sc}(\text{OSO}_2\text{CF}_3)_3$ catalyst, $[1]_0/[2]_0 = 1.54$ without a catalyst, temperature = 100 °C).

In Figure 2, the MALDI-TOF MS results for one set of reaction conditions are shown; the dominating peaks are from the population of macromolecules having two acidic end groups. However, as will be shown in the full article, the proportions of the end groups depend, as could be expected, on the ratio of $[1]_0$ to $[2]_0$, where $[1]_0$ is the initial concentration of ethylene glycol and $[2]_0$ is the initial concentration of phosphoric acid.

As evidenced in Figure 2, oligomers with a polymerization degree up to 11 (i.e., molecular weight ~ 1500) could be detected by MALDI-TOF MS with a typical most probable distribution of molecular masses.

Preliminary kinetic measurements indicate that the rate-determining step of esterification is the formation of poly(phosphoric acid)s. Indeed, this was shown in independent experiments when the rates of poly(phosphoric acid) formation (slow) with the rates of poly(phosphoric acid) reactions with ethylene glycol (fast) were compared. Schematically, the actual course of

polyesterification can be presented as shown in Scheme 1 (although some side reactions are also possible and not shown).

During the next stages of the condensation–polyaddition steps, this sequence of reactions is repeated: presumably the (poly)pyrophosphate function is generated at the monoester chain end, adding then phosphoric acid or the $\dots\text{CH}_2\text{CH}_2\text{OH}$ chain end of another macromolecule.

In some experiments, we observed also the formation of oligo(ethylene glycol)s (mostly di- and tri-) in the macromolecular backbones. These most likely are formed by the wrong addition with nucleophilic attack on the carbon atom, resulting in dealkylation (Scheme 2).

This is only one example of many similar reactions that could proceed at different sites of macromolecules and at different degrees of polymerization. However, in syntheses at lower temperatures, practically no di- or triethylene glycol units in the backbone were observed.

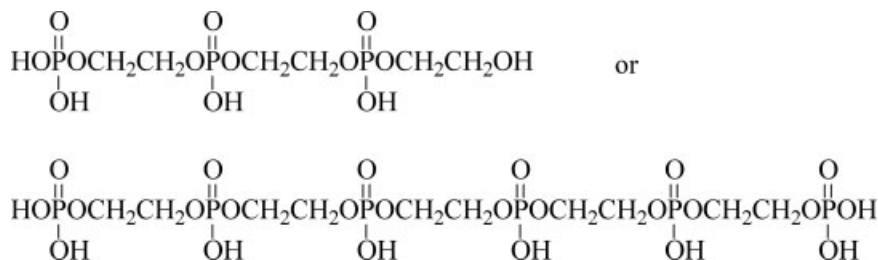
In the presence of catalysts such as $\text{Sc}(\text{CF}_3\text{SO}_3)_3$, the reaction goes faster, although the mechanism of catalytic action is not yet clear. In Figure 3, the formation of the product of the reaction under catalyzed and noncatalyzed conditions is shown. In the presence of the catalyst, the ratio of diester units to monoester units (mostly end groups) grows faster at least at 100 °C and becomes greater than 2:1 (5% of the initial H_3PO_4 is still left), whereas at the same conditions and time without the catalyst, it is much lower.

The ratio 2:1, assuming one or two acidic (monoester) end groups (cf. MALDI-TOF MS, Fig. 2), would mean that the average products may have the structures shown in Scheme 3.

These are idealized average structures. More exact analysis will be given in a full article.

In summary, we have reported that oligo–poly(alkylene phosphate)s can be prepared directly from phosphoric acid and ethylene glycol. The free acidic $\dots\text{OP}(\text{O})(\text{OH})_2$ and/or hydroxy $\dots\text{OCH}_2\text{CH}_2\text{OH}$ end groups can be used for further modification and/or chain extension of other polymers.

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Scheme 3. Average reaction products for a diester/moester ratio of 2:1.

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